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Controlling the Ratio of CZTS to CZTSe Nanocrystals by Hot Injection of Selenium

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In this work, we present a wet-chemical method to prepare CZTS and CZTSe nanoparticles in controlled proportions which will result in a film with desired Se content.

Motivation
We demonstrate precise control in the transformation of CZTS (Cu_2ZnSnS_4) to CZTSe ($Cu_2ZnSnSe_4$) nanoparticles in solution by hot-injection of Se. The proportion of CZTS to CZTSe is determined by the reaction time.

Method: Synthesizing CZTS and CZTSe Nanocrystals
Step 1: CZTS nanocrystals were synthesized using a hot-injection method with oleylamine as the solvent.

Step 2: Se dissolved in TOP (trioctylphosphine) was injected into the solution of CZTS, and CZTSe nanocrystals were formed.

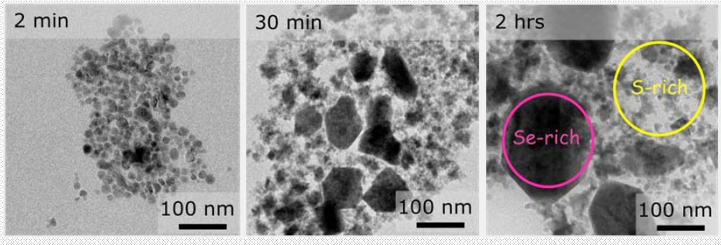
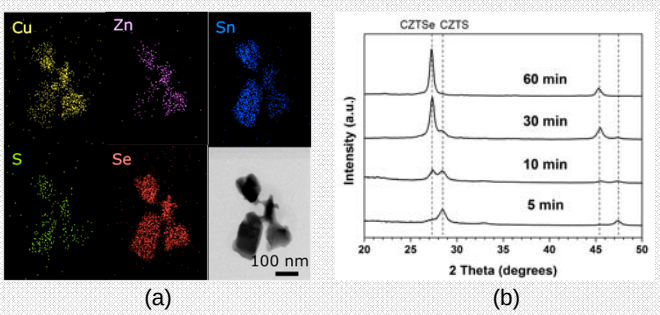
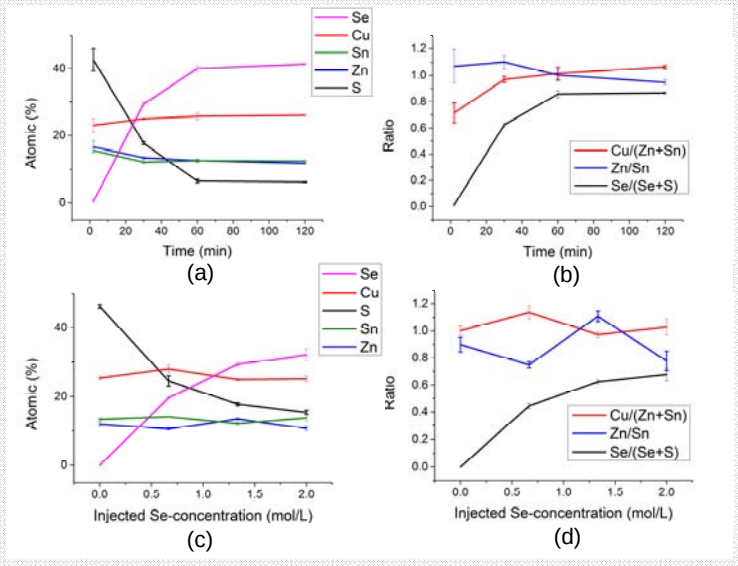


Fig. 1 TEM micrographs of CZTS and CZTSe nanoparticle growth after Se-injection.



(a) (b)

Fig. 2 (a) STEM-EDX elemental mapping of nanocrystals. (b) XRD pattern for CZTS prepared at 220°C for 30 minutes and CZTSe. The diffraction peak positions for CZTS are at 28.48°, 47.43°, and 56.25°. The peaks for CZTSe are at 27.25°, 45.28°, and 53.66°.



Atomic (a) percentages and (b) ratios versus time after Se-injection, at 250°C and 1.33 mol/L Se. Atomic (c) percentages and (d) ratios versus injected Se-concentration, at 250°C after 30 minutes of reaction.

Particle Size TEM micrographs of the nanoparticles after Se-injection are shown in Fig. 1. After Se-injection, the largest particle size evolves from approx. 30 nm after 2 min, to 100 nm after 30 min, and finally 200 nm after 2 hours. Notice the presence of a few large and many small nanoparticles at longer times. The large particles were found to be Se-rich, and the small ones S-rich. Additionally, the distinct faceted shapes of the Se-rich particles imply a highly crystalline material.

Controlled ratios The reaction rate is fastest in the beginning, and saturates after approx. 1 hour.

Transformation STEM-EDX elemental mapping of the nanocrystals, Fig. 2(a), shows evenly distributed atoms. On the contrary, the XRD pattern in Fig. 2(b) indicates that no mixed phase particles are present. The EDX data shows that the ratio of the Se-phase to the S-phase saturates at 80 %, whereas the XRD data indicates 100 % conversion.

Conclusion
On the basis of the experimental data, we propose that the CZTS nanocrystals decompose into ions as Se is injected. Thus an equilibrium of ions in a solution is formed surrounding the solid nanocrystals, and as Se is injected, a quick nucleation and growth occur to form CZTSe nanocrystals.

Acknowledgement
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